Refining in the Future

17.1 INTRODUCTION

In spite of claims to the contrary that are based on the concept of peak oil (Hubbert, 1962), the world is not on the verge of running out of petroleum, heavy oil, or tar sand bitumen (Chapter 1; BP, 2015). However, in spite of the current volatility of petroleum, cheap petroleum may be difficult to obtain in the future as recent price fluctuations have indicated—the causes vary from petroleum being more difficult to obtain from underground formations, especially tight formations (Chapter 1), to the petropolitics of the various oil-producing nations (Speight, 2011a). However, with the entry into the twenty-first century, petroleum refining technology is experiencing great innovation driven by the increasing supply of heavy oils with decreasing quality and the fast increases in the demand for clean and ultraclean vehicle fuels and petrochemical raw materials. As feedstocks to refineries change, there must be an accompanying change in refinery technology. In addition, there will be a need to control the effects of possible changes in crude oil slate on the emissions of carbon dioxide (MathPro Inc., 2013). This means a movement from conventional means of refining heavy feedstocks using (the currently typical) coking technologies to more innovative processes (including hydrogen management) that will produce the ultimate amounts of liquid fuels from feedstocks and maintain emissions within environmental compliance (Penning, 2001; Davis and Patel, 2004; Speight, 2008, 2014a; Farnand et al., 2015).

To meet the challenges from environmentally driven changes over the past five decades from simple crude trends in product slate and the stringent distillation operations into increasingly stringent specifications imposed by environmental complex chemical operations involving legislation, the refining industry in the near future will become increasingly flexible and refined products with specifications that meet innovative with new processing schemes, users requirements (RAROP, 1991; Stratiev and Petkov, 2009; Khan, 2011; Speight, 2011a,b, 2014a). Thus, during the forthcoming decades, the evolution future of petroleum refining and the current refinery configuration (Figure 17.1) will be primarily on process modification with some new innovations coming onstream. The industry will move predictably on to (1) deep conversion of heavy feedstocks, (2) higher hydrocracking and hydrotreating capacity, and (3) more efficient processes.

This chapter presents suggestions and opinions of the means by which refinery processes will evolve during the next three to five decades. This chapter includes material relevant to (1) the comparisons of current feedstocks with heavy oil and bio-feedstocks, (2) the evolution of refineries since the 1950s, (3) the properties and refinability of heavy oil and bio-feedstocks, (4) thermal processes versus hydrosprocesses, and (5) the evolution of products to match the environmental market, with more than a passing mention of the effects of feedstocks from coal and oil shale.

17.2 HISTORY

Refining technology has evolved considerably over the last century in response to changing requirements such as (1) a demand for gasoline and diesel fuel as well as fuel oil, (2) petrochemicals as building blocks for clothing and consumer goods, and (3) more environmentally friendly processes and products.

As a result of this response, the production facilities within the refining industry have become increasingly diverse—process configuration varies from plant to plant according to its size, complexity, and product slate. Moreover, the precise configuration of the refinery of the future is unknown, but it is certain that no two refineries will adapt in exactly the same way. There are
small refineries—1,500–5,000 barrels per day (bpd)—and large refineries that process in excess of 250,000 bpd. Some are relatively simple (Speight, 2014a) and produce only fuels, while other refineries, such as those with integrated petrochemical processing capabilities, are much more complex. Many refineries are part of large integrated oil companies engaged in all aspects of the petroleum technology—from (1) exploration, (2) production, (3) transportation, (4) refining, and (5) marketing of petroleum products. Historically, this has not always been the case. In the early days of the twentieth century, refining processes were developed to extract kerosene for lamps. Any other

FIGURE 17.1  General schematic of a refinery.
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products were considered to be unusable and were usually discarded. A brief history of petroleum refining is presented in the following paragraphs.

In 1861, the first petroleum refinery opened and produced kerosene—a better and cheaper source of light than whale oil—by atmospheric distillation; naphtha and tar (residuum or cracked residuum) produced as by-products. This involved simple batch distillation of crude oil with the objective of maximizing kerosene production. Technological advancements included, first, the introduction of continuous distillation and, then, vacuum distillation—developed in 1870—which greatly facilitated the manufacture of lubricants. The 1890s saw the emergence of the internal combustion engine, creating demand for diesel fuel and gasoline; demand for kerosene declines with the invention and proliferation of the electric light.

Thus, first refining processes were developed to purify, stabilize, and improve the quality of kerosene. However, the invention of the internal combustion engine led (at about the time of World War I) to a demand for gasoline for use in increasing quantities as a motor fuel for cars and trucks. This demand on the lower-boiling products increased, particularly when the market for aviation fuel developed. Thereafter, refining methods had to be constantly adapted and improved to meet the quality requirements and needs of fuels as well as a variety of other products.

Next, the quest for improved lubricants prompted the use of solvent extraction. To make better use of the bottom of the barrel, thermal cracking (in 1913) and visbreaking processes were introduced to crack high molecular weight constituents of the feedstock to produce lower-boiling products. Thermal cracking was developed—in response to increased demand for gasoline due to mass production of automobiles and the outbreak of World War I. This innovation enabled refineries to produce additional gasoline and distillate fuels by subjecting high-boiling petroleum fractions to high pressures and temperatures with the resulting production of lower-boiling, lower-molecular-weight products.

During the 1930s, many advances made to improve gasoline yield and properties as a response to the development of higher-compression engines. This involved the development of processes such as (1) catalytic cracking, thermal reforming, and catalytic polymerization to improve octane number; (2) hydroprocesses to remove sulfur; (3) coking processes to produce gasoline blend stocks; (4) solvent extraction processes to improve the viscosity index of lubricating oil; and (5) solvent dewaxing processes to improve the pour point of the various products. The by-products of these various processes included aromatics, waxes, residual fuel oil, coke, and feedstocks for the manufacture of petrochemicals.

With the onset of World War II and the need for additional supplies of gasoline, the refining industry turned to catalysis for major innovations. Catalytic cracking constituted a step change in the refinery’s ability to convert heavy components into highly valued gasoline and distillates. Wartime demand for aviation fuels helped spur the development of catalytic alkylation processes (which produced blend stocks for high-octane aviation gasoline) and catalytic isomerization (which produced increased quantities of feedstocks for alkylation units) to create high-octane fuels from lighter hydrocarbons. We redistributed hydrogen content among the refinery’s products to improve their properties via catalytic reforming of gasoline, catalytic hydodesulfurization of distillates, and hydrocracking of midrange streams.

The period from the 1950s to the 1970s saw the development of various reforming processes, which also produced blend stocks that were used to improve gasoline quality and yield. Other processes such as deasphalting, catalytic reforming, hydodesulfurization, and hydrocracking are examples of processes developed during this period. In this time period, refiners also started further development of the uses for the waste gases from various processes resulting in the expansion of the petrochemical industry. In the latter part of the period, the industry benefitted from a massive infusion of computer-based quantitative methodology that has significantly improved more control over processes and the composition of products. In addition, automation and control enabled the optimization of unit operation and economic performance.
Thus throughout its history, the refining industry has been the subject of the four major forces that affect most industries and which have hastened the development of new petroleum refining processes: (1) the high demand for liquid fuels such as gasoline, diesel, fuel oil, and jet fuel; (2) uncertain feedstock supply, specifically the changing quality of crude oil and geopolitics between different countries and the emergence of alternate feed supplies such as bitumen from tar sand, natural gas, coal, and the ever-plentiful biomass; (3) increasingly stringent recent environmental regulations in relation to sulfur content of liquid fuels; and (4) continued technology development such as new catalysts and processes.

17.3 REFINERY CONFIGURATIONS

A petroleum refinery is an industrial processing plant that is a collection of integrated process units (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Speight, 2014a). The crude oil feedstock is typically a blend of two or more crude oils, often with heavy oil or even tar sand bitumen blended into a maximum permissible amount, based on the refinery configuration.

17.3.1 PETROLEUM REFINERY

The definition of petroleum (aka crude oil) is often confusing and variable (Chapter 1) and has been made even confusing by the introduction of other terms (such as black oil that only adds color to the nomenclature equation) that add little, if anything to the issues relating to petroleum definitions and terminology (Zittel and Schindler, 2007; Speight, 2008, 2014a). In fact, there are different classification schemes based on (1) economic and/or (2) geological criteria. For example, the economic definition of conventional oil is “conventional oil is oil which can be produced with current technology under present economic conditions.” The problem with this definition is that it is not very precise and changes whenever the economic or technological aspects of oil recovery change. In addition, there are other classifications based on API gravity, such as “conventional oil is crude oil having a viscosity above 17° API.” Moreover, each producing country may change the definitions somewhat for political or economic reasons. However, these definitions do not change the definition stated elsewhere (Chapter 1) that has been used throughout this book.

Recall that the most appropriate definition of tar sands (Chapter 1) is found in the writings of the U.S. government, namely,

Tar sands are the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. The hydrocarbon-bearing rocks are variously known as bitumen-rocks oil, impregnated rocks, oil sands, and rock asphalt.

This definition speaks to the character of the bitumen through the method of recovery. Thus, the bitumen found in tar sand deposits is an extremely viscous material that is immobile under reservoir conditions and cannot be recovered through a well by the application of secondary or enhanced recovery techniques. Mining methods match the requirements of this definition (since mining is not one of the specified recovery methods), and the bitumen can be recovered by alteration of its natural state such as thermal conversion to a product that is then recovered. In this sense, changing the natural state (the chemical composition) as occurs during several thermal processes (such as some in situ combustion processes) also matches the requirements of the definition. Furthermore, by inference and by omission, conventional petroleum and heavy oil are also included in this definition—petroleum is the material that can be recovered by conventional oil well production methods, whereas heavy oil is the material that can be recovered by enhanced recovery methods.
In recent years, the quality of crude oil feedstocks has deteriorated and continues to do so as more heavy oil and tar sand bitumen are being sent to refineries and there is the need for efficient upgrading processes for these feedstocks (Speight, 2005, 2008, 2014a; Rana et al., 2007). This has caused the nature of crude oil refining to be changed substantially, and there has been an increasing need to respond to market demands (market pull) to develop options to upgrade more of the heavy feedstocks, specifically heavy oil and bitumen. In addition, the general trend throughout refining has been to produce more products from each barrel of petroleum and to process those products in different ways to meet the product specifications for use in modern engines. Overall, the demand for gasoline has rapidly expanded and demand has also developed for gas oils and fuels for domestic central heating and fuel oil for power generation, as well as for light distillates and other inputs, derived from crude oil, for the petrochemical industries. However, the means by which a refinery operates in terms of producing the relevant products depends not only on the nature of the petroleum feedstock but also on its configuration (i.e., the number of types of the processes that are employed to produce the desired product slate) that is, in turn, influenced by the specific demands of a market. The refining industry does not dictate the market but must respond to the requirements of the market. Therefore, refineries need to be constantly adapted and upgraded to remain viable and responsive to ever-changing patterns of crude supply and product market demands. As a result, refineries have been introducing increasingly complex and expensive processes to gain higher yields of lower-boiling products from the higher-boiling fractions and residua.

Finally, although mentioned briefly earlier, the yields and quality of refined petroleum products produced by any given oil refinery depend on the mixture of crude oil used as feedstock and the configuration of the refinery facilities. Light/sweet (low-sulfur) crude oil is generally more expensive and has inherent great yields of higher-value low-boiling products such as naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Heavy sour (high-sulfur) crude oil is generally less expensive and produces greater yields of lower-value higher-boiling products that must be converted into lower-boiling products (Speight, 2013a).

Changes in the characteristics of feedstocks to refineries will trigger changes in refinery configurations and corresponding investments. The future crude slate into a refinery is predicted (with a high degree of satisfaction) to consist of larger amounts of heavier sour (high-sulfur) crude oils as well as a shift to higher amounts of extra heavy oil and bitumen, such as the extra heavy oil from the Orinoco Basin (Venezuela) and the nonvolatile carbonaceous material from the tar sand deposits of Alberta (Canada). These changes will require investment in upgrading, either at field level (partial upgrading or full upgrading) to process the extra heavy oil and the tar sand bitumen into pipeline specification synthetic crude oil or at the refinery level (full upgrading) (Figure 17.2; Scouten, 1990; Speight, 2008).

The location of this upgrading capacity (field site or refinery site) will be built is likely to be strongly influenced by market proximity—there are four ways that are currently practiced in bringing heavy crude oil to the market (Hedrick et al., 2006). The first method is to upgrade the material in the oil field and leave much of the material behind as coke and then pipeline the upgraded material out as synthetic crude. A second solution is to build upgrading facilities at an established port area with abundant gas and electric resources. A third solution in common practice is to use traditional crude that is located in the general area to dilute the nontraditional crude to produce an acceptable pipeline material. The final solution is closely related to the established port area solution where a substantial oil field is located far from other fields, from power, or from natural gas. In addition, petroleum refining has grown increasingly complex in the last 40 years. Lower-quality crude oil, crude oil price volatility, and environmental regulations that require cleaner manufacturing processes and higher-performance products present new challenges to the refining industry. Improving processes and increasing the efficiency of energy use are key to meeting the challenges and maintaining the viability of the petroleum refining industry. There is also the need for a refinery to be able to accommodate opportunity crude oils and/or high-acid crude oils (Chapter 1).
Opportunity crude oils are often dirty and need cleaning before refining by the removal of undesirable constituents such as high-sulfur, high-nitrogen, and high-aromatic (such as polynuclear aromatic) components. A controlled visbreaking treatment would clean up such crude oils by removing these undesirable constituents (which, if not removed, would cause problems further down the refinery sequence) as coke or sediment. On the other hand, high-acid crude oils cause corrosion in the atmospheric and vacuum distillation units due to the presence of mineral salts such as magnesium, calcium, and sodium chloride, which are hydrolyzed to produce volatile hydrochloric acid, causing a highly corrosive condition in the overhead heat exchangers (Speight, 2014c). Other contaminants in which are shown to accelerate the hydrolysis reactions are clay minerals and organic acids. In addition to taking preventative measure for the refinery to process these high-margin crude oils without serious deleterious effects on the equipment, refiners will need to develop programs for detailed and immediate feedstock evaluation so that they can understand the qualities of a crude oil very quickly and it can be valued appropriately.

In general, heavy feedstock upgrading will become more and more profitable as recycling and multiple reaction sections will be the prevalent technology trends. Several process innovations have been introduced in the form of varying process options, some using piggyback techniques (where one process works in close conjunction with another process) that will fit into the future refinery (Speight, 2011b). Such process options will continue to be developed, and many refiners will accept the piggyback concept for heavy feedstock upgrading. Another significant improvement in the heavy feedstock conversion technologies will be in catalyst design. Hydrocracking catalysts used in ebullated-bed processes will continue to require multifunctionality. The transition metal sulfides such as molybdenum (Mo), cobalt (Co), and nickel (Ni) will still remain the industry favorites, because of their excellent hydrogenation, hydodesulfurization (HDS), and hydrodenitrogenation (HDN) activities, as well as their availability and cost. However, greater attention will be paid to the size of the particles, pore volume and size distribution, pore diameter, and the shape of the particles to maximize the utilization of the catalyst.

The catalyst technology known as metals trapping technology will continue to improve and allow higher levels of heavy feedstocks to be processed while reducing hydrogen yields and lowering coke yields. As feedstocks deteriorate in quality and metals’ content of the feed is higher, the need for such catalyst design will be a major factor in resid upgrading. In addition, the use of scavenger additives such as metal oxides may also see a surge in use. As a simple example, a metal oxide (such as calcium oxide) has the ability to react with sulfur-containing feedstock to produce a
hydrocarbon (and calcium sulfide) followed by oxidative reservation to the oxide and, for example, conversion of the sulfur dioxide to sulfur trioxide and thence to sulfuric acid:

\[
\text{S}_{\text{Feedstock}} + \text{CaO} \rightarrow \text{Hydrocarbon product} + \text{CaS} + \text{H}_2\text{O}
\]

\[
\text{CaS} + \text{O}_2 \rightarrow \text{CaO} + \text{SO}_2
\]

\[
\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3
\]

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3
\]

The precise configuration of the refinery of the future is unknown but, because of feedstock variation and the makeup of feedstock blends, it is certain that no two refineries will adapt in exactly the same way. However, the evolution of the refinery of the future will not be strictly confined to petroleum-based processes but will be based on a variety of feedstocks (Speight, 2011b). This will be solved in refinery of the future with the development of deep conversion processing, such as heavy feedstock hydrocracking and the inclusion of processes to accommodate other feedstocks (RAROP, 1991; Khan and Patmore, 1998; Rispoli et al., 2009; Motaghi et al., 2010a, b; Speight, 2014a).

Moreover, the future of the petroleum refining industry will be primarily on processes for the production of improved quality products. In addition to heavy ends deep conversion, there will also be changes in the feedstock into a refinery. Biomass, liquids from coal, and liquids from oil shale will increase in importance (Bajus, 2010; Demirbaş, 2010, 2011; Speight, 2013b; Syngellakis, 2015a, b). These feedstocks (1) will be sent to refineries or (2) processed at a remote location and then blended with refinery stocks are options for future development and the nature of the feedstocks. Above all, such feedstock must be compatible with refinery feedstocks and not cause fouling in any form.

The basic refining process for the conversion of residua, heavy oil, and tar sand bitumen to lower-boiling saleable products and the conversion of distillation residues consist of cracking the feedstock constituents to increase the hydrogen content and to decrease the carbon content of the derived products (Speight, 2011b, 2014a). While such processes will continue (at least) for the next 50 years and even throughout the remainder of the twenty-first century (Speight, 2011b), many refineries are investigating the potential large-scale utilization of biomass as partial feedstocks. For practical reasons, small-capacity refineries might be the first to attempt such uses of biomass in a biopetroleum refinery complex. Biomass might be used in the form of preprepared pellets (obtained from agriculture residues such as forestry residues, corn stock, and straw) as a feedstock blend with heavy oil. The approach could produce benefits such as (1) improvement in the quality of the final market products and of the economics of the entire activity, (2) positive impact on rural development (new jobs and new income for farmers), and (3) decrease in carbon dioxide emissions by the substitution of renewable biomass and conversion to hydrocarbon products (Grassi, 2004).

Moreover, it is more than likely that the future refinery will have a gasification section devoted to the conversion of coal and biomass to Fischer–Tropsch hydrocarbons—perhaps even with rich oil shale added to the gasifier feedstock. Many refineries already have gasification capabilities (for the production of hydrogen), but the trend will increase to the point (over the next two decades) where nearly all refineries feel the need to construct a gasification section to handle heavy petroleum-related feedstocks and refinery waste as well as nonpetroleum-related carbonaceous feedstocks such as coal, biomass, and nonrefinery waste material (Chapter 14; Speight, 2014b).

Coal gasification is a tried-and-true technology and there has been a move in recent years to feedstocks other than coal (Speight, 2013b, 2014b). Among other alternative energy conversion pathways, biomass gasification has great potential because of its flexibility to use a wide range
of feedstocks and to produce energy and a wide range of fuels and chemicals (Kumar et al., 2009). Recently, the focus of its application has changed from the production of combined heat and power to the production of liquid transportation fuels. The technical challenges in commercialization of fuels and chemicals production from biomass gasification include increasing the energy efficiency of the system and developing robust and efficient technologies for cleaning the product gas and its conversion to valuable fuels and chemicals. Thus, future energy production (as conventional petroleum reserves continue to decline) is likely to involve coprocessing alternative energy sources in which petroleum residua/heavy oil/extra heavy oil/tar sand bitumen is processed with other energy sources and requires a new degree of refinery flexibility as the key target, especially when related to the increased use of renewable energy sources such as biomass (Szkló and Schaeffer, 2005).

### 17.3.2 Biorefinery

Whatever the rationale and however the numbers are manipulated, the supply of crude oil, the basic feedstock for refineries and for the petrochemicals industry, is finite and supply/demand issues will continue to deplete petroleum reserves. Although the supply of heavy oil, extra heavy oil, and tar sand bitumen can be moved into the breach, the situation can be further mitigated to some extent by the exploitation of more technically challenging fossil fuel resources and the introduction of new technologies for fuels and chemicals production from coal and oil shale (Scouten, 1990; Speight, 2011a,b, 2013b; Lee et al., 2014). In addition, there is a substantial interest in the utilization of plant-based matter (biomass) as a raw material feedstock for the chemicals industry (Marcilly, 2003; Lynd et al., 2005; Huber and Corma, 2007; Lynd et al., 2009). Plants accumulate carbon from the atmosphere via photosynthesis and the widespread utilization of these materials as feedstocks for the generation of power, fuels, and chemicals.

In terms of the use of plant matter as energy-producing feedstocks, there are two terms that need to be defined and these are (1) biomass and (2) biofuels. Biomass is a renewable energy source—unlike the fossil fuel resources: petroleum, coal, and natural gas—and is derived from recently living organisms or their metabolic by-products. An advantage of fuel from biomass (biofuel), in comparison to most other fuel types, is it is biodegradable and thus relatively harmless to the environment if spilled. Typically, a biofuel is any fuel that is derived from biomass but has been further defined as any fuel with a minimum content (≥80% v/v) of materials derived from living organisms harvested within the 10 years preceding its manufacture.

Plants offer a unique and diverse feedstock for energy production and for the production of chemicals. Plant biomass can be gasified to produce synthesis gas—a basic chemical feedstock for the production of hydrocarbons and also a source of hydrogen for a future hydrogen economy (Chapter 15; Chadeesingh, 2011). More generally, biomass feedstocks are recognized (and/or defined) by the specific chemical content of the feedstock or the manner in which the feedstock is produced (Speight, 2008). For example, primary biomass feedstocks that are currently being used for bioenergy include grains and oilseed crops used for transportation fuel production, plus some crop residues (such as orchard trimmings and nut hulls) and some residues from logging and forest operations that are currently used for heat and power production (Table 17.1). In the future, it is anticipated that a larger proportion of the residues inherently generated from food crop harvesting, as well as a larger proportion of the residues generated from ongoing logging and forest operations, will be used for bioenergy. Secondary biomass feedstocks differ from primary biomass feedstocks in that the secondary feedstocks are a by-product of processing of the primary feedstocks. Specific examples of secondary biomass include sawdust from sawmills, black liquor (which is a by-product of paper making), and cheese whey (which is a by-product of cheese-making processes). Vegetable oils used for biodiesel that are derived directly from the processing of oilseeds for various uses are also a secondary biomass resource. Tertiary biomass feedstocks include fats, greases, oils, construction and demolition wood debris, other waste wood from the urban environments, as well as
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packaging wastes, municipal solid wastes, and landfill gases. A category other wood waste from the urban environment includes trimmings from urban trees.

The simplest, cheapest, and most common method of obtaining energy from biomass is direct combustion. Any organic material, with a water content low enough to allow for sustained combustion, can be burned to produce energy, which can be used to provide space or process heat, water heating, or (through the use of a steam turbine) electricity. In the developing world, many types of biomass such as animal dung and agricultural waste materials are burned to produce heat for cooking and warmth. In fact, such organic residues can also be used for energy production through conversion by natural biochemical processes as well as through the auspices of a biorefinery.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to the petroleum refinery, which produce multiple fuels and products from petroleum. In addition to applying biological methods to petroleum itself such as the (1) desulfurization of fuels, (2) denitrogenation of fuels, (3) removal of heavy metals, (4) transformation of heavy crudes into light crudes, and (5) the biodegradation and bioremediation of petroleum spills as well as spills of petroleum products (Le Borgne and Quintero, 2003; Bhatia and Sharma, 2006; Speight and Arjoon, 2012; El-Gendy and Speight, 2015), biorefining offers a key method to accessing the integrated production of chemicals, materials, and fuels. While the biorefinery concept is analogous to that of an oil refinery in terms of feedstock pretreatment, conversion to products, and product finishing (Figure 17.3), there are significant differences—particularly in the character and properties of the respective feedstocks.

While the primary function of a biorefinery is to produce biofuels, there are also options to use biomass in various refinery scenarios (Speight, 2011c; Lee et al., 2014). The biomass could be supplied by anything from corn, sugarcane, grasses, wood, and soybeans to algae. In place of fossil fuel–based hydrocarbon or hydrocarbonaceous feedstocks, biomass offers sugars, starches, fats, and proteins. Some chemicals will be synthesized using enzymes or genetically engineered microorganisms, and some will be produced using the inorganic catalysts used in traditional chemical processes. Throughout the decision process, consideration must be given to the use of biomass-derived chemicals without perturbing food supplies.

A biorefinery would (in a manner similar to the petroleum refinery) integrate a variety of conversion processes to produce multiple product streams and would combine the essential technologies to transform biological raw materials into a range of industrially useful intermediates. However, there

### TABLE 17.1
Heating Value of Selected Fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>23,000</td>
</tr>
<tr>
<td>Gasoline</td>
<td>20,000</td>
</tr>
<tr>
<td>Crude oil</td>
<td>18,000</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>16,000</td>
</tr>
<tr>
<td>Coal (anthracite)</td>
<td>14,000</td>
</tr>
<tr>
<td>Coal (bituminous)</td>
<td>11,000</td>
</tr>
<tr>
<td>Wood (farmed trees, dry)</td>
<td>8,400</td>
</tr>
<tr>
<td>Coal (lignite)</td>
<td>8,000</td>
</tr>
<tr>
<td>Biomass (herbaceous, dry)</td>
<td>7,400</td>
</tr>
<tr>
<td>Biomass (corn stover, dry)</td>
<td>7,000</td>
</tr>
<tr>
<td>Wood (forest residue, dry)</td>
<td>6,600</td>
</tr>
<tr>
<td>Bagasse (sugarcane)</td>
<td>6,500</td>
</tr>
<tr>
<td>Wood</td>
<td>6,000</td>
</tr>
</tbody>
</table>
may be the need to differentiate the type of biorefinery on the basis of the feedstock. For example, a crop biorefinery would use raw materials such as cereals or maize and a lignocellulose biorefinery would use raw material with high cellulose content, such as straw, wood, and paper waste. In addition, a variety of methods and techniques can be employed to obtain different product portfolios of bulk chemicals, fuels, and materials (Speight, 2008, 2011c). Biotechnology-based conversion processes can be used to ferment the biomass carbohydrate content into sugars that can then be further processed. An alternative is to employ thermochemical conversion processes that use pyrolysis or gasification of biomass to produce a hydrogen-rich synthesis gas, which can be used in a wide range of chemical processes (Chadeesingh, 2011). On the other hand, the use of bio-feedstocks in a conventional petroleum refinery cannot be ignored, whether or not they are used as gasifier feedstocks (Chapter 14; Speight, 2008, 2011c, 2014a,b).

These inherent characteristics and limitations of biomass feedstocks have focused the development of efficient methods of chemically transforming and upgrading biomass feedstocks in a refinery (Figure 17.3). The refinery would be based on two platforms to promote different product slates: (1) the biochemical platform and (2) the thermochemical platform. Using this two-train approach and by analogy with crude oil, every element of the plant feedstock will be utilized including the low-value lignin components. However, the different compositional nature of the biomass feedstock, compared to crude oil, will require the application of a wider variety of processing tools in the biorefinery. Processing of the individual components will utilize conventional thermochemical operations and state-of-the-art bioprocessing techniques.

The biorefinery concept provides a means to significantly reduce production costs such that a substantial substitution of petrochemicals by renewable chemicals becomes possible. However, significant technical challenges remain before the biorefinery concept can be realized.

### 17.3.3 Coal Liquids Refinery

Refinery feedstocks from coal (coal liquids) have not been dealt with elsewhere in this text, but descriptions are available from other sources (Speight, 2013b). Coal conversion and product refining (into liquids) are not a new concept and were used during World War II as a means of producing military fuels by the German government.
Technically, the Bergius process was one of the early processes for the production of liquid fuels from coal. In the process, lignite or subbituminous coal is finely ground and mixed with heavy oil recycled from the process. Catalyst is typically added to the mixture, and the mixture is pumped into a reactor. The reaction (which uses catalysts containing tungsten, molybdenum, tin, or nickel) occurs at between 400°C and 500°C (750°F and 930°F) and 3,000 and 10,000 psi hydrogen and produces gas, aromatic naphtha, light gas oil, and heavy gas oil:

\[ n\text{C}_{\text{coal}} + (n + 1)\text{H}_2 \rightarrow C_n\text{H}_{2n+2} \]

The different fractions can be sent to a refinery for further processing to yield synthetic fuel or a fuel blending stock of the desired quality. The composition of coal liquids produced from coal depends very much on the character of the coal and on the process conditions and, particularly, on the degree of hydrogen addition to the coal. In fact, current concepts for refining the products of coal liquefaction processes have relied, for the most part, on already-existing petroleum refineries, although it must be recognized that the acidity (i.e., phenol content) of the coal liquids and their potential incompatibility with conventional petroleum (including heavy oil) may pose new issues within the refinery system (Speight, 2008, 2013b, 2014a).

The other category of coal liquefaction processes invokes the concept of the indirect liquefaction process—a two-stage conversion operation—in which the coal is first converted (by reaction with steam and oxygen, at temperatures in excess of 800°C/1470°F) to a gaseous mixture composed primarily of carbon monoxide and hydrogen (syngas). The gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products. The synthesis of hydrocarbons from carbon monoxide and hydrogen (synthesis gas) (the Fischer–Tropsch synthesis) is a procedure for the indirect liquefaction of coal to produce a range of hydrocarbon products (Speight, 2008, 2013b, 2014b; Chadeesingh, 2011):

\[ \text{[C]}_{\text{coal}} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]
\[ n\text{CO} + (2n + 1)\text{H}_2 \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O} \]

These reactions result primarily in low- and medium-boiling aliphatic compounds suitable for blending with similar boiling-range products to gasoline and diesel fuel. Synthesis gas can also be converted to methanol, which can be used as a fuel, fuel additive, or further processed into gasoline via the Mobil M–gas process. In terms of liquids from coal that can be integrated into a refinery, this represents the most attractive option and does not threaten to bring on incompatibility problems as can occur when phenols are present in the coal liquids. While such a scheme is not meant to replace other fuel-production systems, it would certainly be a fit into a conventional refinery—gasification is used in many refineries to produce hydrogen (Chapter 15) and a gasification unit is part of the flexicoking process (Chapter 8).

### 17.3.4 Shale Oil Refinery

The processes for producing liquids (shale oil) from oil shale involve heating (retorting) the shale to convert the organic kerogen to a raw shale oil (Scouten, 1990; Speight, 2008). There are two basic oil shale retorting approaches: (1) mining followed by retorting at the surface and (2) in situ retorting, that is, heating the shale in place underground (Vinegar et al., 2010). A similar process can be applied to tar sand formation in which the temperature is controlled and is analogous to visbreaking (Karanikas et al., 2009). Retorting essentially involves thermal decomposition (at temperatures in excess of 485°C/>900°F) of the kerogen with simultaneous removal of distillate in the absence
of oxygen. During the process, the initial products can then decompose (depending on the process parameters) into lower-weight hydrocarbon molecules.

The shale oil so produced contains a large variety of hydrocarbon compounds but also has high nitrogen content compared to a nitrogen content of 0.2%–0.3% w/w for a typical petroleum that can affect refinery operations (Scouten, 1990; Speight, 2008, 2013a, 2014a). In addition, shale oil also has a high olefin and diolefin content, and it is the presence of these olefins and diolefins in conjunction with high nitrogen content that gives shale oil the tendency to form insoluble sediment. Crude shale oil also contains appreciable amounts of arsenic, iron, and nickel that interfere with refining. Upgrading, or partial refining, to improve the properties of a crude shale oil may be carried out using different options—depending upon the composition and the origin of the shale oil (Scouten, 1990)—and hydrotreating is the option of choice to produce a stable product (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Speight, 2014a). In terms of refining and catalyst activity, the nitrogen content of shale oil is a disadvantage and, if not removed, the arsenic and iron in shale oil will poison and foul the supported catalysts used in hydrotreating. In terms of the use of shale oil residua as a modifier for asphalt, where nitrogen species can enhance binding with the inorganic aggregate, the nitrogen content is beneficial (Speight, 2015).

In general, oil shale distillates have a much higher concentration of high-boiling-point compounds that would favor the production of middle distillates (such as diesel and jet fuels) rather than naphtha. Oil shale distillates also had a higher content of olefins, oxygen, and nitrogen than crude oil, as well as higher pour points and viscosities. Aboveground retorting processes tended to yield a lower API gravity oil than the in situ processes (a 25° API gravity was the highest produced). Additional processing equivalent to hydrocracking would be required to convert oil shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating.

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**FIGURE 17.4** Products from synthesis gas.
17.3.5 GASIFICATION REFINERY

The concept of using other feedstocks to blend with petroleum feedstocks bring to the fore the concept of a gasification refinery, which would use gasification technology as is the case of the Sasol refinery in South Africa (Chadeesingh, 2011). The manufacture of mixtures of carbon monoxide and hydrogen has been an important part of chemical technology for approximately a century. Originally, such mixtures were obtained by the reaction of steam with incandescent coke and were known as water gas. Eventually, steam reforming processes, in which steam is reacted with natural gas (methane) or petroleum naphtha over a nickel catalyst, found wide application for the production of synthesis gas.

The gasification refinery would produce synthesis gas (from the carbonaceous feedstock) from which liquid fuels would be manufactured using the Fischer–Tropsch synthesis technology (Couvaras, 1997; Speight, 2008, 2014b; Chadeesingh, 2011; Luque and Speight, 2015). Synthesis gas is used as a source of hydrogen or as an intermediate in producing hydrocarbons via the Fischer–Tropsch synthesis (Figure 17.4). Indeed, as petroleum supplies decrease, the desirability of producing gas from other carbonaceous feedstocks will increase.

17.4 THE FUTURE REFINERY

There is no one single upgrading solution that fits all refineries and the varied crude oil slates. Thus, a careful evaluation of the slate of feedstocks into the refinery is necessary and is not always a simple undertaking for an existing refinery.

The evaluation typically starts at the time of selection of the feedstocks that adequately fit the configuration of the refinery, which varies from refinery to refinery. Some refineries may be more oriented toward the production of gasoline (large reforming and/or catalytic cracking), whereas the configuration of other refineries may be more oriented toward the production of middle distillates such as jet fuel and gas oil. Over the past four decades, the refining industry has been challenged by changing feedstocks and product slate that has introduced a high degree of flexibility with improved technologies and improved catalysts.

However, the evolution of the refinery of the future will not be strictly confined to petroleum processes. The major consequence will be a much more environmentally friendly product quality. These will be solved in refinery of the future, the refinery beyond 2020 with the development of deep conversion processing, such as residue hydrocracking and the inclusion of processes to accommodate other feedstocks. The panacea (rather than a Pandora’s box) for a variety of feedstocks could well be the gasification refinery (Speight, 2011b). This type of refinery approaches that of a petrochemical complex, capable of supplying the traditional refined products, but also meeting much more severe specifications, and petrochemical intermediates such as olefins, aromatics, hydrogen, and methanol. Furthermore, as already noted earlier, integrated gasification combined cycle (IGCC) can be used to raise power from feedstocks such as vacuum residua and cracked residua (in addition to the production of synthesis gas), and a major benefit of the integrated gasification combined cycle concept is that power can be produced with the lowest sulfur oxide ($\text{SO}_x$) and nitrogen oxide ($\text{NO}_x$) emissions of any liquid/solid feed power generation technology.

The success of current operations notwithstanding, the challenges facing the refining industry will focus on the diversity of the feedstocks. Even within the petroleum family of feedstocks where elemental analysis varies over a relatively narrow range, changes to refining technology are required to produce the optimum yield of desired products. Another unique foreseeable disruption coming to the industry is the anticipated inclusion of biomass feedstocks and the changes that this will bring to refining. Indeed, much of the intellectual property embodied in the current refinery operations will have to change as wide variations in feedstock composition occur and attempts are made to produce the necessary hydrocarbon fuels from a wide variety of biomass feedstocks. Any yet, the
reﬁning industry will survive—being one of the most resilient industries to commence operations during the past 150 years.

The reﬁning industry can be regarded as unique insofar as very few industries have to deal with a feedstock-product chain beginning at a natural resource that has to be recovered from a subterranean formation and proceed through the application of a variety of processes all the way through to the end use consumer. Furthermore, it is imperative for reﬁners to raise their operations to new levels of performance. Merely extending current process performance incrementally will most likely fail to meet most future performance goals. To do this, it will be necessary to reshape reﬁning technology to be more adaptive to changing feedstocks and product demand and to explore the means by which the technology and methodology of reﬁnery operations can be translated not only into increased proﬁtability but also into survivability.

Part of the future growth will be at or near heavy crude and bitumen production sites to decrease heavy crude viscosity and improve the quality to ease transportation and open markets for crudes of otherwise marginal value. Visbreaking may be considered to be a conversion process rather than a process to produce fuel oil that meets speciﬁcations. Coking can be improved by reducing hydrocarbon gas formation and by inhibiting the formation of polynuclear aromatic products that are produced by the process and which are not inherent to the feedstock. Both of these processes would beneﬁt if a higher-valued product could be produced.

To this end, hydroconversion (Chapters 10 and 11) will continue to be a necessary and economically justiﬁable part of a residue conversion project. The use of ebullated-bed reactors for hydroconversion is evolving as is the use of slurry-catalyst systems. In addition, the gasiﬁcation of heavy feedstocks moving closer to the time when it will be a ready choice for the conversion of heavy feedstocks transportation fuels. Heavy feedstocks conversion projects (including power generation using waste streams) could move into positive economics in regions with high local power demand. Moreover, with the ever-increasing and stringent speciﬁcations for reﬁnery products, reﬁners will continue to make efforts to improve the heavy feedstock processing technologies that convert the heavy feedstock into valuable and environment-friendly products. Currently, a variety of residue hydrocracking processes using ﬁxed-bed, moving-bed, or ebullated-bed reactors are available. Furthermore, the economics of the slurry bed processing technology indicates an attractive rate of returns with the existing crude oils and product price structure (Rispoli et al., 2009).

Several process innovations have been introduced in the form of varying process options, some using piggyback techniques (where one process is operative in close conjunction with another process) that will fit into the future reﬁnery. Another signiﬁcant improvement in the hydroprocessing technologies will be in catalyst design. This follows from recognition that a novel catalyst is one of

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Group Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C2</td>
<td>Synthetic natural gas (SNG)</td>
</tr>
<tr>
<td>C3–C4</td>
<td>Liqueﬁed petroleum gas (LPG)</td>
</tr>
<tr>
<td>C5–C7</td>
<td>Light petroleum</td>
</tr>
<tr>
<td>C8–C10</td>
<td>Heavy petroleum</td>
</tr>
<tr>
<td>C11–C20</td>
<td>Middle distillate</td>
</tr>
<tr>
<td>C11–C12</td>
<td>Kerosene</td>
</tr>
<tr>
<td>C13–C20</td>
<td>Diesel</td>
</tr>
<tr>
<td>C21–C30</td>
<td>Soft wax</td>
</tr>
<tr>
<td>C31–C60</td>
<td>Hard wax</td>
</tr>
</tbody>
</table>
Refining in the Future

reasonable design and integration of the active, supporting, and promoting components that allow an optimal combination of activity, surface area, and pore diameter, giving the highest activity.

High-conversion refineries will move to the gasification of feedstocks for the development of alternative fuels and to enhance equipment usage. A major trend in the refining industry market demand for refined products will be in synthesizing fuels from simple basic reactants (e.g., synthesis gas) when it becomes uneconomical to produce superclean transportation fuels through conventional refining processes. Fischer–Tropsch plants together with IGCC systems will be integrated with or even into refineries, which will offer the advantage of high-quality products (Table 17.2; Stanislaus et al., 2000; Shires et al., 2010).

REFERENCES


